

## PORT DOCUMENTATION PAGE

AD-A221 829

## 1b. RESTRICTIVE MARKINGS

None

## 3. DISTRIBUTION/AVAILABILITY OF REPORT

Unlimited

## 2b. DECLASSIFICATION/CONTINUING AVAILABILITY

## 4. PERFORMING ORGANIZATION REPORT NUMBER(S)

interim technical report #37

## 5. MONITORING ORGANIZATION REPORT NUMBER(S)

## 6a. NAME OF PERFORMING ORGANIZATION

Department of Chemistry

6b. OFFICE SYMBOL  
(if applicable)

## 7a. NAME OF MONITORING ORGANIZATION

Office of Naval Research

## 6c. ADDRESS (City, State, and ZIP Code)

Massachusetts Institute of Technology  
77 Mass. Avenue, Bldg. 6-335  
Cambridge, MA 02139

## 7b. ADDRESS (City, State, and ZIP Code)

Chemistry Division  
800 N. Quincy Street  
Arlington, VA 222178a. NAME OF FUNDING/SPONSORING  
ORGANIZATION

Office of Naval Research

8b. OFFICE SYMBOL  
(if applicable)

## 9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

N00014-84-K-0553

## 8c. ADDRESS (City, State, and ZIP Code)

Chemistry division  
800 N. Quincy Street  
Arlington, VA 22217

## 10. SOURCE OF FUNDING NUMBERS

PROGRAM  
ELEMENT NO.PROJECT  
NO.TASK  
NO.WORK UNIT  
ACCESSION NO.

051-579

## 11. TITLE (Include Security Classification)

Electrochemical Behavior of the Oxide Formed by Reduction of  $\text{RuO}_4^{2-}$ ...

## 12. PERSONAL AUTHOR(S)

D.F. Lyons, M.O. Schloh, J.J. Hickman, and M.S. Wrighton

## 13a. TYPE OF REPORT

technical interim

## 13b. TIME COVERED

FROM 5/89 TO 5/90

## 14. DATE OF REPORT (Year, Month, Day)

5/16/90

## 15. PAGE COUNT

47

## 16. SUPPLEMENTARY NOTATION

Prepared for publication in Chemistry of Materials

## 17. COSATI CODES

FIELD GROUP SUB-GROUP

## 18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

ruthenium oxide, microelectrochemical transistor

## 19. ABSTRACT (Continue on reverse if necessary and identify by block number)

See Attached Sheet

## 20. DISTRIBUTION/AVAILABILITY OF ABSTRACT

☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USER

## 21. ABSTRACT SECURITY CLASSIFICATION

Unlimited

## 22a. NAME OF RESPONSIBLE INDIVIDUAL

Mark S. Wrighton

## 22b. TELEPHONE (Include Area Code)

617-253-1597

## 22c. OFFICE SYMBOL

DTIC  
EXTRACT  
MAY 25 1990  
S E D

### ABSTRACT

Properties of macroscopic electrodes and arrays of closely spaced ( $1.2\ \mu\text{m}$ ) Au microelectrodes ( $\sim 2\ \mu\text{m}$  wide  $\times$   $50\ \mu\text{m}$  long  $\times$   $0.1\ \mu\text{m}$  high) coated with the oxide ( $\text{RuO}_x$ ) derived from reduction of  $\text{RuO}_4^{2-}$  in  $1\ \text{M}$  NaOH are reported. XPS data show  $\text{RuO}_x$  consists of a mixture of Ru oxidation states with significant amounts of  $\text{Ru}^{\text{IV}}$ .  $\text{RuO}_x$  exhibits a well defined cyclic voltammetric wave centered at about  $0.0\ \text{V}$  vs. SSCE in pH 7.0 solution. The average of the anodic and cathodic peak current positions is taken to be  $E^0$  for the  $\text{Ru}^{\text{IV/III}}$  couple. The position, shape and area of the wave at a given pH are insensitive to electrolyte composition for buffered solutions of LiCl, NaCl,  $\text{CaCl}_2$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NaClO}_4$ , Na(acetate), Na(tosylate), or Na(phosphate). A pH dependence of  $\sim 71\ \text{mV/pH}$  unit from pH = 2 to pH = 14 is found for this wave. UV-vis spectroelectrochemistry shows four broad absorption bands in reduced  $\text{RuO}_x$ . Oxidation increases absorbance across the entire visible spectrum. Electrical connection of microelectrodes by  $\text{RuO}_x$  was verified by cyclic voltammetry. The steady state resistance of  $\text{RuO}_x$  films has been measured as a function of potential and was typically found to vary from  $\sim 10^9$  ohms for the reduced film to  $\sim 10^6$  ohms for the film at potentials  $\sim 100\ \text{mV}$  positive of  $E^0$ . At more positive potentials, film resistance increases. The minimum resistance corresponds to a resistivity of approximately  $300\ \text{ohm-cm}$ . The potential at which minimum resistance occurs has a  $71\ \text{mV/pH}$  unit dependence, but the

magnitude of the minimum resistance is not affected by pH. RuO<sub>x</sub>-based microelectrochemical transistors can amplify power, but the maximum frequency (~0.1 Hz) is limited by the slow oxidation and reduction of RuO<sub>x</sub> films. A pair of microelectrodes connected by RuO<sub>x</sub> functions as a pH-sensitive microelectrochemical transistor and detection of a change of pH in a flowing stream was demonstrated. A model is proposed for the structure of RuO<sub>x</sub> consisting of a relatively ordered lattice domain surrounded by oxoruthenium moieties.



Accession For	
NTIS GRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/ _____	
Availability Codes	
Dist	Avail and/or Special
A-1	

Office of Naval Research  
Contract NOOO14-84-K-0553  
Task No. 051-597  
Technical Report #37

Electrochemical Behavior of the Oxide Formed by Reduction of  $\text{RuO}_4^{2-}$ :  
A pH-Dependent Ruthenium Oxide-Based  
Microelectrochemical Transistor

by

Donald F. Lyons, Martin O. Schloh, James J. Hickman

and Mark S. Wrighton

Prepared for Publication

in

Chemistry of Materials

Massachusetts Institute of Technology  
Department of Chemistry  
Cambridge, MA 02139

Reproduction in whole or in part is permitted for any purpose of the  
United States Government.

This document has been approved for public release and sale; its  
distribution is unlimited.

[Prepared for publication as an article in  
Chemistry of Materials]

**Electrochemical Behavior of the Oxide Formed by  
Reduction of  $\text{RuO}_4^{2-}$ : A pH-Dependent Ruthenium Oxide-Based  
Microelectrochemical Transistor**

Donald F. Lyons, Martin O. Schloh, James J. Hickman, and  
Mark S. Wrighton\*

*Department of Chemistry  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139*

\* Address correspondence to this author.

### ABSTRACT

Properties of macroscopic electrodes and arrays of closely spaced ( $1.2\ \mu\text{m}$ ) Au microelectrodes ( $\sim 2\ \mu\text{m}$  wide  $\times$   $50\ \mu\text{m}$  long  $\times$   $0.1\ \mu\text{m}$  high) coated with the oxide ( $\text{RuO}_x$ ) derived from reduction of  $\text{RuO}_4^{2-}$  in  $1\ \text{M}$  NaOH are reported. XPS data show  $\text{RuO}_x$  consists of a mixture of Ru oxidation states with significant amounts of  $\text{Ru}^{\text{IV}}$ .  $\text{RuO}_x$  exhibits a well defined cyclic voltammetric wave centered at about  $0.0\ \text{V}$  vs. SSCE in pH 7.0 solution. The average of the anodic and cathodic peak current positions is taken to be  $E^0$  for the  $\text{Ru}^{\text{IV}}/\text{III}$  couple. The position, shape and area of the wave at a given pH are insensitive to electrolyte composition for buffered solutions of LiCl, NaCl,  $\text{CaCl}_2$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NaClO}_4$ , Na(acetate), Na(tosylate), or Na(phosphate). A pH dependence of  $\sim 71\ \text{mV/pH}$  unit from pH = 2 to pH = 14 is found for this wave. UV-vis spectroelectrochemistry shows four broad absorption bands in reduced  $\text{RuO}_x$ . Oxidation increases absorbance across the entire visible spectrum. Electrical connection of microelectrodes by  $\text{RuO}_x$  was verified by cyclic voltammetry. The steady state resistance of  $\text{RuO}_x$  films has been measured as a function of potential and was typically found to vary from  $\sim 10^9$  ohms for the reduced film to  $\sim 10^6$  ohms for the film at potentials  $\sim 100\ \text{mV}$  positive of  $E^0$ . At more positive potentials, film resistance increases. The minimum resistance corresponds to a resistivity of approximately  $300\ \text{ohm-cm}$ . The potential at which minimum resistance occurs has a  $71\ \text{mV/pH}$  unit dependence, but the

magnitude of the minimum resistance is not affected by pH.  $\text{RuO}_x$ -based microelectrochemical transistors can amplify power, but the maximum frequency ( $\sim 0.1$  Hz) is limited by the slow oxidation and reduction of  $\text{RuO}_x$  films. A pair of microelectrodes connected by  $\text{RuO}_x$  functions as a pH-sensitive microelectrochemical transistor and detection of a change of pH in a flowing stream was demonstrated. A model is proposed for the structure of  $\text{RuO}_x$  consisting of a relatively ordered lattice domain surrounded by oxoruthenium moieties.

We wish to report the characterization of an electrodeposited ruthenium oxide and its use as the device active material in a microelectrochemical transistor. In connection with microelectrochemical devices  $\text{RuO}_x$  is unique because it is useful over a wide pH range (2-14) and its "conductivity" vs. potential is similar to that of a conventional redox polymer showing a well-defined peak at a potential that depends on pH. Ruthenium oxides are currently of immense importance as electrocatalysts and have been studied extensively.<sup>1</sup> Ruthenium oxides formed by electrolysis of a solution species, however, have not been investigated in depth. Anderson and Warren described a route to an electrodeposited ruthenium oxide by oxidation of  $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{OH}_2)_3^{2+}$ ,<sup>2</sup> and Lam et al. reported the formation of a black precipitate upon reduction of  $\text{RuO}_4^{2-}$ .<sup>3</sup> We have examined the oxide formed upon reduction of  $\text{RuO}_4^{2-}$  in order to understand the behavior of ruthenium oxide-based microelectrochemical transistors. In particular, we report the potential dependence of conductivity and the pH dependence of the electrochemical response. Additionally, aspects of morphology, composition, and spectroelectrochemistry are reported. Throughout this paper, the oxide derived from reduction of  $\text{RuO}_4^{2-}$  will be referred to as  $\text{RuO}_x$ .

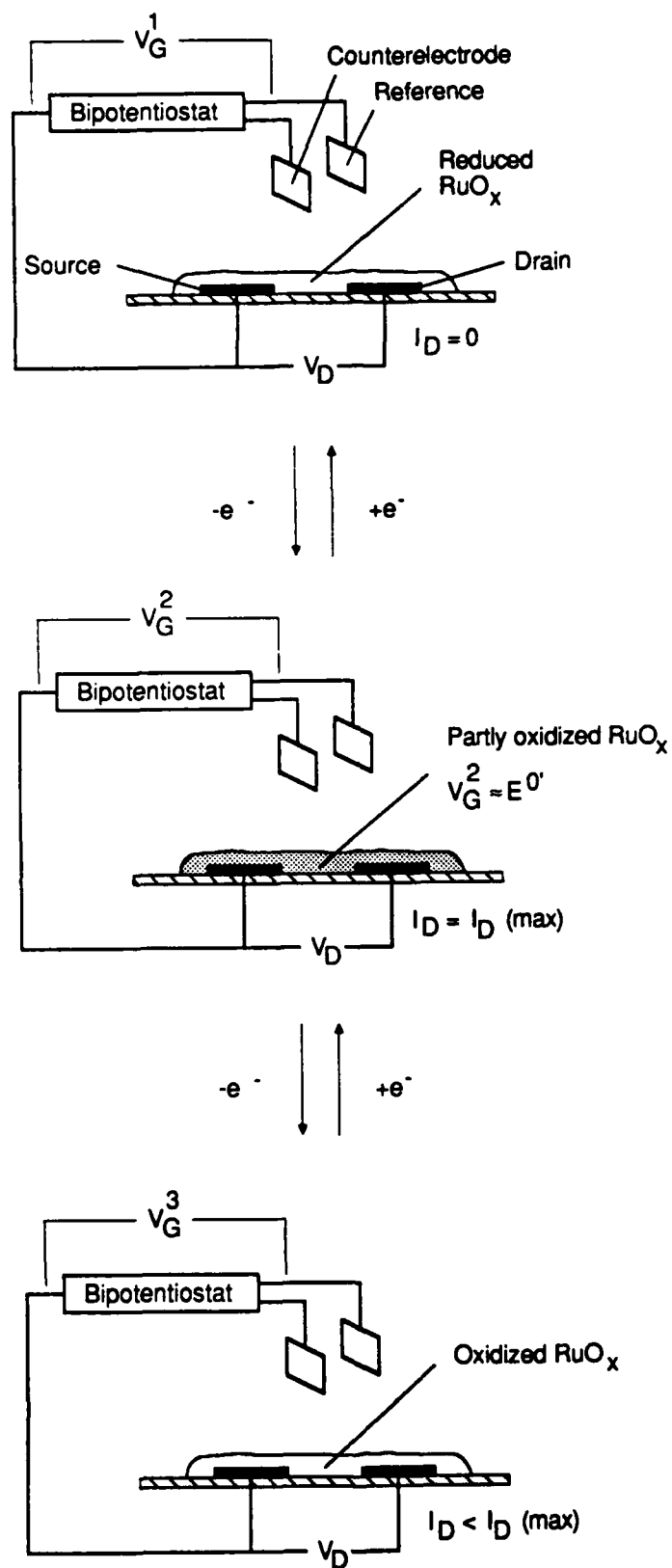
Closely spaced (1.2  $\mu\text{m}$ ) microelectrodes (~2  $\mu\text{m}$  wide by ~50  $\mu\text{m}$  long by ~0.1  $\mu\text{m}$  high) are useful for studying the potential dependence of the conductivity of  $\text{RuO}_x$ .



Conductivity studies of  $\text{Ni(OH)}_2$ <sup>4</sup> and  $\text{WO}_3$ <sup>5</sup> films, as well as the organic conducting polymers polyaniline,<sup>6</sup> polypyrrole,<sup>7</sup> and poly(3-methylthiophene),<sup>8</sup> have been accomplished on such microelectrodes. Microelectrochemical transistors based on these materials have already been demonstrated.<sup>4-8</sup> It is important to note that materials with a conductivity that varies with electrochemical potential are necessary for the operation of microelectrochemical transistors. Materials that exhibit a constant conductivity at all potentials (for example, the oxide formed upon pyrolysis of  $\text{RuCl}_3$ )<sup>9</sup> cannot be used as the basis for such an electrochemical device. We will demonstrate that  $\text{RuO}_x$  does indeed exhibit a potential-dependent conductivity and that pH sensitive microelectrochemical transistors can be constructed with  $\text{RuO}_x$ .

Scheme I illustrates the operation of a microelectrochemical device based on  $\text{RuO}_x$ . A  $\text{RuO}_x$  film covers and electrically connects two adjacent microelectrodes.  $V_G$ , the gate voltage, establishes the state of charge of the  $\text{RuO}_x$  film. The current associated with the faradaic processes controlled by  $V_G$  is the gate current,  $I_G$ . A small potential difference,  $V_D$ , or the drain potential, can be maintained between the two microelectrodes. The more negative electrode is called the source and the more positive electrode the drain, by analogy to transistor nomenclature.<sup>10</sup> The current flowing between the microelectrodes is the drain current,  $I_D$ , and reflects

the conductivity of the  $\text{RuO}_x$  film for a particular  $V_G$ . When  $V_G$  equals  $V_G^1$ , where  $\text{RuO}_x$  is insulating, no current flows in the drain circuit:  $I_D = 0$ . When  $V_G$  is moved to a potential at which  $\text{RuO}_x$  is partially oxidized,  $V_G^2$ , the  $\text{RuO}_x$  is a better conductor and current flows in the drain circuit,  $I_D > 0$ , for a nonzero  $V_D$ . The maximum  $I_D$  obtained from a  $\text{RuO}_x$ -based device is at a  $V_G^2$  which is near the peak potential of the cyclic voltammetry wave for the  $\text{RuO}_x$ . When  $V_G$  is moved to a potential at which  $\text{RuO}_x$  is fully oxidized,  $V_G^3$ , again  $I_D > 0$ , but  $I_D$  is found to be less than that obtained at  $V_G^2$ . Microelectrochemical transistors resemble solid-state transistors, but a key difference is that in a solid state device  $I_G$  is a capacitive current,<sup>10</sup> rather than a faradaic current associated with electrochemistry. A second significant difference for the  $\text{RuO}_x$ -based device is that the  $I_D$ - $V_G$  characteristic shows a well-defined maximum at a  $V_G$  that depends on the pH of the medium to which the device is exposed.



**Scheme 1.** RuO<sub>x</sub>-based microelectrochemical transistor.

## EXPERIMENTAL SECTION

$K_2RuO_4 \cdot 2H_2O$  (Alfa) was used as received and stored in a controlled atmosphere chamber under  $N_2$ . All other chemicals as well as the  $SnO_2$ -coated glass were used as received from commercial sources.

Electrochemical instrumentation consisted of Pine Instruments RDE 4 Bipotentiostats with Kipp and Zonen BD 91 XY-Y-T recorders for microelectrode experiments, and an ECO 551 potentiostat controlled by a PAR 175 programmer with a Houston Instruments 2000 XY recorder for macroscopic electrode experiments. An SSCE (sodium chloride-saturated calomel electrode) was used as reference and all potentials quoted are vs. SSCE.

Spectroelectrochemistry was monitored on a Hewlett Packard 8451A rapid-scan spectrometer. Thickness measurements were made with a Tencor Instruments Alpha Step 100 surface profiler with a  $12.5 \mu m$  radius stylus and a tracking force of 5 mg. Flowing streams were produced and delivered to microelectrodes using the pumps of a Hewlett Packard 1084-B liquid chromatograph. Scanning electron micrographs were obtained on a Hitachi S 800 instrument. Auger electron spectra were obtained on a Physical Electronics 660 Scanning Auger Microprobe. X-ray photoelectron spectra were obtained on a Physical Electronics 584 spectrometer or on a Surface Science Laboratories SSX-100 spectrometer and signals were referenced to C 1s at 284.6 eV.

Microelectrodes used in these experiments were of a design previously described.<sup>4-8</sup> Each chip consists of an array of eight parallel Au or Pt microelectrodes on an insulating layer of  $\text{Si}_3\text{N}_4$ , surrounded by macroscopic contact pads. Each microelectrode was 50  $\mu\text{m}$  long, 2.4  $\mu\text{m}$  wide, and 0.1  $\mu\text{m}$  thick, and electrode separation was 1.2  $\mu\text{m}$ . Insulation over all Au or Pt except for the microelectrodes and contact pads was either an additional layer of  $\text{Si}_3\text{N}_4$  or epoxy. Cleaning and testing of microelectrodes followed previously published procedures.<sup>6-8</sup>

$\text{RuO}_x$  deposition was done using a freshly prepared 5 mM  $\text{K}_2\text{RuO}_4$ /1 M NaOH solution. A two-compartment cell was used with the counter electrode separated from the working and reference electrodes. Cycling a macroscopic working electrode at 100 mV/s between -0.2 and -0.8 V led to the growth of a film of  $\text{RuO}_x$  associated with a cyclic voltammetry wave centered at -0.54 V. Gentle washing of the electrode after  $\text{RuO}_x$  deposition removed loosely bound particles, but did not affect the voltammetric signal. Deposition of  $\text{RuO}_x$  onto microelectrode arrays was performed in the same manner as on to macroscopic electrodes. Microelectrodes which were to be left underivatized were held at +0.1 V during the deposition procedure.

## RESULTS

**a. Microscopy, Auger Mapping, and Qualitative Aspects of Electrochemical Behavior of  $\text{RuO}_x$ .** Deposition of  $\text{RuO}_x$  films is based on the literature procedure.<sup>3</sup> Electrode composition does not seem to be important, as we have successfully derivatized glassy carbon,  $\text{SnO}_2$ , Au, and Pt electrodes. Films of up to  $0.5\text{ }\mu\text{m}$  thick have been prepared as measured by profilometry and SEM data. Films of this thickness are somewhat fragile and can be removed by vigorous washing, but  $1000\text{ }\text{\AA}$  thick films are extremely durable. Figure 1 shows a scanning electron micrograph of a  $\text{RuO}_x$  film deposited on Pt. The  $\text{RuO}_x$  appears granular and is also punctuated with larger holes which expose more oxide underneath. Unlike the oxide formed on Ru electrodes<sup>11</sup> or that formed by pyrolyzed  $\text{RuCl}_3$ ,<sup>9</sup> both of which have a fairly compact morphology,  $\text{RuO}_x$  appears porous and nonuniform.

An Auger electron element map of a microelectrode array for which the central four electrodes had been derivatized and the other four electrodes were kept underivatized reveals that Ru is present on the central electrodes and absent on the outer electrodes, Figure 2. Interestingly, Ru signals were seen on the area surrounding the electrode array. This is consistent with a mechanism for  $\text{RuO}_x$  deposition in which  $\text{Ru}^{2+}$  is first reduced to a soluble  $\text{Ru}^{\text{IV}}$  species which subsequently decomposes to the insoluble  $\text{RuO}_x$ .<sup>3</sup> The small size of individual microelectrodes permits the soluble  $\text{Ru}^{\text{IV}}$  species to diffuse away and decompose on

electroinactive areas of the chip. The Auger map in Figure 2, however, establishes that it is possible to selectively modify the microelectrode array by controlling the potential of electrodes to remain free of  $\text{RuO}_x$ .

The cyclic voltammetry of the  $\text{RuO}_x$  film is depicted in Figure 3 and shows a wave centered at 0.0 V at pH 7. X-ray photoelectron spectroscopy (XPS) of  $\text{RuO}_x$  films has been used in an attempt to determine the Ru oxidation states of the  $\text{RuO}_x$  at different electrochemical potentials. An  $\text{RuO}_x$  film withdrawn from a pH 7.5 Na phosphate solution at -0.5 V shows a broad Ru  $3d_{5/2}$  signal at 282.0 eV which indicates a mixture of Ru oxidation states.<sup>12</sup> The binding energy of  $\text{RuO}_x$  is very close to that reported for  $\text{RuO}_2$ <sup>12b</sup> indicating that Ru is present as at least the +4 oxidation state. Unfortunately,  $\text{RuO}_x$ -derivatized electrodes withdrawn from the pH 7.5 solution at 0.0 and 0.35 V give almost the same XPS Ru  $3d_{5/2}$  peak as found for the sample withdrawn at -0.5 V results. It is possible that a degree of surface oxidation of  $\text{RuO}_x$  occurs when the reduced  $\text{RuO}_x$  is removed from solution and transferred to the XPS spectrometer, preventing clear distinction between the Ru  $3d_{5/2}$  binding energies of the three  $\text{RuO}_x$  samples. The XPS results, therefore, do not better define the Ru oxidation states, and we adopt the earlier  $\text{Ru}^{\text{IV/III}}$  assignment for the wave centered at ~0.0 V at pH = 7.<sup>3</sup> Further oxidation of  $\text{RuO}_x$  beyond the peak in the cyclic voltammetry, which begins at +0.35 V in pH 7.0 solution, is assigned to the  $\text{Ru}^{\text{VI/IV}}$

couple.<sup>3</sup> At more positive potentials, the oxidation process overlaps  $\text{H}_2\text{O}$  oxidation to give  $\text{O}_2$  evolution. Cycling  $\text{RuO}_x$  to the potential of  $\text{O}_2$  evolution results in gradual film dissolution and loss of electroactivity. However, the film is remarkably durable as long as the electrode potential is not moved more than 0.2 V positive of the peak of the cyclic voltammetry wave. In one experiment a  $\text{RuO}_x$ -derivatized electrode was cycled for 18 h between +0.3 and -0.5 V in pH 7.5 solution with less than 5% loss in the area of the  $\text{RuO}_x$  voltammogram. At potentials negative of the  $\text{Ru}^{\text{IV/III}}$  wave, the  $\text{RuO}_x$  film shows no faradaic activity until  $\text{H}_2$  evolution occurs.  $\text{H}_2$  oxidation current is not observed in the reverse sweep. A slight capacitive current is observed between the  $\text{H}_2$  evolution and the  $\text{Ru}^{\text{IV/III}}$  wave indicating that the film is not totally insulating in this potential regime (*vide infra*). Prolonged  $\text{H}_2$  evolution does not affect the  $\text{Ru}^{\text{IV/III}}$  voltammogram.

The voltammetry of the electrodeposited  $\text{RuO}_x$  film resembles that of the film produced upon oxidation of  $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{OH}_2)_3^{2+}$ .<sup>2</sup> In contrast, ruthenium oxide films produced by pyrolysis of  $\text{RuCl}_3$ <sup>9</sup> or by Ru anodization<sup>13-15</sup> exhibit large capacitive currents with only small faradaic waves present. Ruthenium oxides formed by pyrolysis or anodization have electrochemical behavior<sup>9,13-15</sup> which resembles porous metallic electrodes with high conductivity and have very high surface area as deduced from the large double layer capacitance.<sup>1,16</sup> Apparently,  $\text{RuO}_x$  films



deposited from solution behave electrochemically in a manner similar to conventional redox polymers.<sup>17</sup> The integral of the cyclic voltammogram, coupled with measurements of  $\text{RuO}_x$  thickness, show that the oxidation/reduction associated with the wave at 0.0 V at pH = 7.0 involves  $>100 \text{ C/cm}^3$ . This is similar to the charge density for conventional redox polymers.<sup>17</sup> It should be noted, though, that the electrodeposited  $\text{RuO}_x$  films described here are much better conductors (*vide infra*) than simple redox polymers such as those derived from viologens.<sup>18</sup>

Consistent with chemical changes in the  $\text{RuO}_x$  films upon oxidation and reduction,  $\text{RuO}_x$  exhibits electrochromism in the UV-vis region. Figure 4 shows spectroelectrochemistry of a  $\text{RuO}_x$ -coated  $\text{SnO}_2$  electrode. The reduced  $\text{RuO}_x$  exhibits five absorption bands centered at 332, 374, 440, 548, 738 nm. Changing the electrode potential to more positive potentials increases absorbance across the entire spectrum. The actual UV-vis spectra appears to show no clearly defined new bands upon oxidation of the  $\text{RuO}_x$  film. However, the difference UV-vis does show broad new bands at 402, 454, 580 and 800 nm. Similar electrochromic behavior is found in solutions with a pH of 4.3 or 9.6.

**b. pH and Electrolyte Dependence of Cyclic Voltammetry of  $\text{RuO}_x$ .**  $\text{RuO}_x$  electrochemistry is pH dependent; the average of the anodic and cathodic peaks,  $E^0'$ , for  $\text{Ru}^{\text{IV/III}}$  varies by 71 mV/pH unit from pH 2 to pH 14 as shown in Figure 5. In unbuffered solutions the voltammetric waves become poorly

defined. The pH dependence of  $E^0$  indicates that slightly more than one proton is lost from the film for every electron that is withdrawn (approximately 7  $H^+$  per 6  $e^-$ ). The pH dependence is similar for both NaCl and  $NaNO_3$  supporting electrolytes. This type of non-Nernstian pH behavior has been observed in the voltammetry of several hydrous metal oxides (Ni,<sup>19</sup> Ir,<sup>20</sup> Rh,<sup>21</sup> Au,<sup>22</sup> Pd<sup>23</sup>) as well as in thermally prepared  $RuO_2$ .<sup>24</sup> This effect is usually attributed to the acid-base properties of the oxides. For example, proton loss from coordinated water molecules may occur upon oxidation due to the higher positive charge on the central metal atoms.<sup>25</sup>

We have studied cation and anion effects on the  $RuO_x$  electrochemistry. 0.05 M buffer/1.0 M electrolyte solutions were prepared. For cations, a pH 4.0 Na(acetate) buffer was used with LiCl, NaCl,  $CaCl_2$ , or  $NH_4Cl$  as the supporting electrolyte. For anions, a pH 7.0 Na(phosphate) buffer was used with NaCl,  $NaClO_4$ , or Na(tosylate) as supporting electrolyte. Additionally, a pH 7.5, 0.5 M Na(phosphate) solution was examined. No change in the shape, area, or position of the  $RuO_x$  voltammogram (5 mV/s) for a fixed pH was seen. These results indicate that, in general,  $RuO_x$  is insensitive to electrolyte composition as long as the solution pH is maintained by a buffer.

**c. Scan Rate Dependence of Cyclic Voltammetry.** The relationship of the voltammetric peak current to the scan rate is a widely used technique to determine the charge

transport properties of chemically modified electrodes.<sup>17</sup> A linear increase of peak current with increasing sweep rate is expected for very fast charge transport and a fall off from such a linear response signals kinetic sluggishness. We have examined the peak current vs. scan rate behavior of  $\text{RuO}_x$ -coated Pt electrodes. It is recognized that this method may be affected by uncompensated ohmic drop through the film, by the rate of electron exchange between the film and the electrode, or by localized pH changes at high scan rates.<sup>26</sup> The data, Figure 6, show qualitatively better charge transport through  $\text{RuO}_x$  at low pHs. At low scan rates no pH effect is observed on peak current, but the higher scan rates reveal slow oxidation in basic solutions. AC impedance results on anodically and thermally grown ruthenium oxides were interpreted as showing proton motion to be important in the conduction mechanism,<sup>27</sup> but this does not provide insight into why low pH results in faster oxidation. The  $\text{RuO}_x$  film thickness may slightly shrink under acidic conditions due either to neutralization of anionic moieties in the film or formation of hydrogen bonds between oxyruthenium centers.

We have also characterized the cyclic voltammetry of  $\text{RuO}_x$  on microelectrode arrays.  $\text{RuO}_x$  is deposited on the arrays by the same procedure used for macroscopic electrodes. The cyclic voltammetry of four adjacent Au microelectrodes derivatized with  $\text{RuO}_x$  is shown in Figure 7. At 20 mV/s sweep rate the area of the cyclic voltammogram of

all four electrodes driven together is essentially the same as that of the individual electrodes. This indicates that there is an electrical connection between the microelectrodes via  $\text{RuO}_x$  such that at 20 mV/s nearly all of the  $\text{RuO}_x$  is electrically accessible from any one of the four derivatized microelectrodes. If there were no connection, the area of the cyclic voltammogram of the four microelectrodes driven together would be the sum of the individual voltammograms. The cyclic voltammograms at 50 mV/s in Figure 7 do show that not all the  $\text{RuO}_x$  is accessible by addressing any one electrode. The difference between the data for the 20 and 50 mV/s sweep rate is due to the relatively sluggish charge transport in the  $\text{RuO}_x$ . At very slow scan rates, <10 mV/s, all  $\text{RuO}_x$  accessible to one microelectrode is accessible to another  $\text{RuO}_x$ -connected microelectrode. Similar behavior has been reported for  $\text{WO}_3$ - and  $\text{Ni}(\text{OH})_2$ -derivatized microelectrode arrays.<sup>4,5</sup>

**d. Potential Dependence of the  $\text{RuO}_x$  Resistance.** An important property of  $\text{RuO}_x$  is its resistance as a function of its electrochemical potential. This property can be measured using two microelectrodes connected by a  $\text{RuO}_x$  film. Like previously characterized microelectrochemical devices, the change in resistance of  $\text{RuO}_x$  is associated with the injection or withdrawal of charge through an electrochemical redox process. Measurement of the resistance entails bringing adjacent,  $\text{RuO}_x$ -connected electrodes to a given potential,  $V_G$ , waiting until redox equilibrium is

established, and slowly scanning the potential of one microelectrode by a small amount around  $V_G$ , while holding the adjacent electrode at  $V_G$ . With  $\text{RuO}_x$ -connected microelectrodes, measurements were made ~5 minutes after moving to a new  $V_G$ . Changes in resistance are observed by varying  $V_G$  through the region where redox processes occur. The current passing between the electrodes was measured and related to the resistance by Ohm's law.

The data in Figure 8 show that the resistance of  $\text{RuO}_x$ -connected microelectrodes varies by about three orders of magnitude, from  $\sim 10^9$  ohms to  $\sim 10^6$  ohms, as  $V_G$  is varied from -0.4 to 0.1 V, in pH 7.5 solution. At more positive potentials, film resistance actually increases by an order of magnitude. A similar resistance minimum has been observed for polyaniline-<sup>6</sup> and poly(3-methylthiophene)-<sup>8b</sup> connected microelectrodes. Such behavior is expected for conventional redox polymer-based microelectrochemical transistors.<sup>28</sup> The resistance minimum seen for  $\text{RuO}_x$ -connected microelectrodes is pH-dependent, and occurs ~100 mV positive of the peak in the cyclic voltammogram for  $\text{RuO}_x$  at a given pH. The measured resistance of different samples of  $\text{RuO}_x$  may vary from the data in Figure 8 by up to an order of magnitude, but the change in resistance for a particular sample never varies by more than three orders of magnitude. The minimum resistance of  $\text{RuO}_x$ -connected microelectrodes is much higher than for polyaniline, polypyrrole, or poly(3-methylthiophene) derivatized onto microelectrodes.<sup>6-8</sup> In

the insulating state the resistance, as for  $\text{WO}_3^5$  and  $\text{Ni}(\text{OH})_2^4$ , is lower than for the conducting organic polymers. The point is that the  $\text{RuO}_x$  shows only a ~1000-fold change in conductivity and is always moderately conducting. The low resistance for  $\text{RuO}_x$  in the "insulating" state gives rise to the small charging currents observed negative of the peak in the cyclic voltammetry.

The resistance of  $\text{RuO}_x$ -connected microelectrodes *per se* is not especially meaningful information, as it can only be referenced to the resistance of other redox-active electronic conductors derivatized on closely spaced microelectrodes of the same geometry. Unlike the resistance, the resistivity,  $\rho$ , defined in equation (1), is a characteristic property of a material.

$$R = \rho (l/A) \quad (1)$$

In equation (1),  $l$  is the length of a uniform conductor, and  $A$  is its cross sectional area. Assuming complete uniformity of  $\text{RuO}_x$  films, an approximate calculation of the resistivity can be made using the well-defined microelectrode geometry. For typical  $\text{RuO}_x$ -based devices, the 50  $\mu\text{m}$  long microelectrodes are covered with a 0.5-1.0  $\mu\text{m}$  thick film. The length is taken to be the 1.2  $\mu\text{m}$  spacing between microelectrodes. Calculations indicate that in the maximum conducting state, the resistivity of electrochemically deposited  $\text{RuO}_x$  is 200-400  $\Omega\text{-cm}$ . This value is about equal

to the resistivity of moderately doped single crystal semiconductors,<sup>10</sup> but much larger than conventional redox polymers such as polyviologens.<sup>18</sup> The sample to sample variability in resistance is probably a result of differences in  $\text{RuO}_x$  film thickness rather than in resistivity. While the resistivity of  $\text{RuO}_x$  may be high for a "conducting" material, it is the potential dependence of the resistivity that leads to interesting consequences in connection with microelectrochemical transistors.

**e. Transistor Properties of  $\text{RuO}_x$ -Connected Microelectrode Arrays.**

It has been established that redox materials that undergo large changes in resistance upon redox cycling can be used in transistor-like devices as the active switching material.<sup>4-8</sup> We have characterized the transistor properties of  $\text{RuO}_x$ -based microelectrochemical transistors. As expected from the relatively high resistance of the conducting state, the response times and amplification properties of devices based on the  $\text{RuO}_x$  films are not as good as those of devices based on materials such as poly(3-methylthiophene) and polyaniline which can amplify power at frequencies approaching 100 kHz.<sup>29</sup> However,  $\text{RuO}_x$  is durable over a wider pH range than other materials used to prepare pH-sensitive microelectrochemical transistors.

Based on the resistance data in Figure 8 and the configuration represented in Scheme I, when  $V_G$  is moved from  $V_G^1$ , where  $\text{RuO}_x$  is reduced, to  $V_G^2$ , where  $\text{RuO}_x$  is partially oxidized, and there is a potential difference  $V_D$  between two

adjacent microelectrodes,  $I_D$  can be expected to go from close to zero to a finite value that depends on the magnitude of  $V_D$ . Figure 9 shows  $I_D$  vs. time for a  $\text{RuO}_x$ -based transistor where  $V_G$  is stepped from  $-0.50$  to  $+0.05$  V and back in a pH 7.5 solution. With  $V_D = 100$  mV,  $I_D$  shifts reproducibly from zero at  $V_G = -0.50$  V to  $140$  nA at  $V_G = 0.1$  V. The limiting  $I_D$  for the  $100$  mV  $V_D$  implies a resistance of approximately  $7.1 \times 10^5 \Omega$  at  $V_G = 0.1$  V. The device takes approximately  $10$  s to achieve a steady state  $I_D$ . The current spikes upon scan reversal are indicative of the charging (or gate) current,  $I_G$ , necessary to turn the device on and off. While the magnitude of  $I_D$  is limited at fixed  $V_D$  by the  $\text{RuO}_x$  resistance (and therefore  $V_G$ ), the rate at which a particular  $I_D$  is attained is limited by the rate of faradaic processes associated with switching the  $\text{RuO}_x$  between different states of charge.

Evidence that  $\text{RuO}_x$ -based microelectrochemical transistors function as electrical power amplifiers is illustrated in Figure 10, which shows the magnitudes and relationships of  $V_G$ ,  $I_G$ , and  $I_D$ , for a slow triangular  $V_G$  variation between  $-0.35$  and  $+0.05$  V in pH 7.0 buffer. The average power amplification,  $\underline{A}$ , is given by equation (2).

$$\underline{A} = \frac{\text{average power in the drain circuit}}{\text{average power in the gate circuit}} \quad (2)$$



For the data shown in Figure 11,  $\underline{A}$  is equal to 1.8. In theory, at the same frequency and surface coverage, differences in the amplification ability of microelectrochemical transistors depend on the maximum conductivity of the materials used to connect adjacent microelectrodes. We find the observed amplification properties for devices prepared from redox active metal oxides and the conducting polymers accurately reflect the relative maximum conductivities of the materials. Power amplification is intrinsically frequency dependent in that  $I_G$  increases with scan rate. Furthermore, at sufficiently high frequencies, limitations in rates of faradaic processes preclude complete turn on/turn off. The data in Figure 10 are obtained in the mHz frequency domain, while polyaniline-based microelectrochemical transistors with similar electrode geometry can amplify power at frequencies approaching 1 kHz.<sup>29a</sup> The slow operating speed of  $\text{RuO}_x$ -based microelectrochemical transistors is limited by the slow electrochemistry of the  $\text{RuO}_x$  films. At frequencies higher than ~1 Hz, the  $\text{RuO}_x$ -based transistors do not amplify power, i.e.  $\underline{A} < 1$ .

Figure 11 illustrates the steady state current voltage characteristics of a  $\text{RuO}_x$ -based microelectrochemical transistor.  $V_D$  is fixed at 100 mV and  $V_G$  is slowly scanned across the potential regime of interest. This  $\text{RuO}_x$  transistor was examined in three solutions of differing pH. We find essentially no difference in the maximum obtainable

$I_D$  from pH to pH. The potential at which  $I_D$  is a maximum occurs ~100 mV positive of the peak of the cyclic voltammogram in the same electrolyte and shifts by 71 mV/pH unit. Since  $I_D$  depends on the charge transport properties of  $\text{RuO}_x$ , these steady state data agree with the cyclic voltammetry results, at slow scan rates, on macroscopic electrodes.

The pH-dependent nature of the  $I_D$ - $V_G$  curves serves as the basis for a pH sensor, Figure 12. A  $\text{RuO}_x$  transistor was placed in the effluent stream of an HPLC and the pH of the stream varied from 5.5 to 7.3.  $V_G$  was fixed at 0.0 V and  $V_D$  was set at 100 mV. At this  $V_G$ ,  $\text{RuO}_x$  is poorly conducting in pH 5.5 solution, but is much more conducting in pH 7.3 solution. Accordingly,  $I_D$  for this device is high in pH 7.3 and low in pH 5.5. The  $\text{RuO}_x$ -based device is durable and maintains nearly constant  $I_D$  values over five hours of operation. The use of a  $\text{RuO}_x$ -based transistor is constrained at a fixed  $V_G$  by  $\text{H}_2$  evolution at lower pH's and by the degradation at potentials ~0.2 V more positive of the peak of the cyclic voltammetry wave. However, the stability of  $\text{RuO}_x$  over a wide pH range is a considerable improvement over  $\text{WO}_3$ - and  $\text{Ni}(\text{OH})_2$ -based transistors<sup>4,5</sup> which fail in basic and acidic media respectively.

## DISCUSSION

Reduction of  $\text{RuO}_4^{2-}$  (ruthenium tetraoxide ion) in alkaline solution results in deposition of an oxide,  $\text{RuO}_x$  exhibiting characteristics intermediate between "redox conducting" and "electronically

conducting" materials. Like a conventional redox polymer,  $\text{RuO}_x$  shows a well-defined cyclic voltammetry wave and a conductivity maximum at a potential close to the peak of the wave.<sup>28</sup> However, conductivity values obtained for  $\text{RuO}_x$  are much closer to those obtained for electronically conducting polymers and metal oxides. The  $E^0$  of  $\text{RuO}_x$  is pH-sensitive, 71 mV/pH unit in the pH range of 2-14. These properties allow the demonstration of a  $\text{RuO}_x$ -based pH sensitive microelectrochemical transistor having a pH-dependent  $I_D$  maximum in a  $I_D$  vs.  $V_G$  plot and which is durable over a wide pH range (2-14). Additionally, the redox properties of the  $\text{RuO}_x$  allow the demonstration of a pH-dependent microelectrochemical diode.<sup>30</sup>

We believe that the electrochromism, voltammetry, conducting maximum, and the large "background" conductivity of  $\text{RuO}_x$  can be explained by the following model. As depicted in Figure 13, the structure of  $\text{RuO}_x$  may consist of domains of a relatively ordered ruthenium-oxygen lattice surrounded by electroinactive oxoruthenium moieties. The UV-Vis absorption spectrum of  $\text{RuO}_x$  is a combination of absorption bands that are essentially unaffected by the state of charge of the  $\text{RuO}_x$  from the oxoruthenium moieties, and bands that grow in upon oxidation of the ruthenium-oxygen networks. The redox process in  $\text{RuO}_x$  probably involves gain and loss of either protons or hydroxide groups from the ruthenium-oxygen network. It follows that while the electrolyte must be buffered to observe a well-defined

$\text{RuO}_x$  voltammetric wave, the particular electrolyte composition has no effect on this wave. In addition, the absence of specific electrolyte effects on  $\text{RuO}_x$  voltammetry suggests that the electroactive networks are open and porous. Such porous structures have been postulated for other hydrous metal oxides.<sup>25</sup> The magnitude of the resistivity of  $\text{RuO}_x$  implies some degree of electron delocalization and the existence of an electronic band. As  $\text{RuO}_x$  is oxidized or reduced this band is emptied of or filled with, electrons, and the partially filled band exhibits the highest conductivity. The heterogeneous structure of  $\text{RuO}_x$  limits the maximum conductivity by limiting electron mobility, but also introduces enough localized states, which can accept or donate electrons, to give a residual conductivity even when  $\text{RuO}_x$  is fully reduced.

**Acknowledgements.** We thank the Office of Naval Research and Defense Advanced Research Projects Agency for partial support of this research. We also acknowledge support from the National Science Foundation Materials Research Laboratory at M.I.T.

## REFERENCES

1. Trasatti, S.; O'Grady, W. E. In *Advances in Electrochemistry and Electrochemical Engineering*; Gerischer, H., and Tobias, C. W., Eds.; Wiley: New York, **1981**; Vol. 12, p 177.
2. Anderson, D. P.; Warren, L. F. *J. Electrochem. Soc.* **1984**, 131, 347.
3. Lam, K. W.; Johnson, K. E.; Lee, D. G. *J. Electrochem. Soc.* **1978**, 125, 1069.
4. Natan, M. J.; Bélanger, D.; Carpenter, M. K.; Wrighton, M. S. *J. Phys. Chem.* **1987**, 91, 1834.
5. Natan, M. J.; Mallouk, T. E.; Wrighton, M. S. *J. Phys. Chem.* **1987**, 91, 648.
6. Paul, E. W.; Ricco, A. J.; Wrighton, M. S. *J. Phys. Chem.* **1985**, 89, 1441.
7. Kittlesen, G. P.; White, H. S.; Wrighton, M. S. *J. Amer. Chem. Soc.* **1984**, 106, 7389.
8. (a) Thackeray, J. T.; White, H. S.; Wrighton, M. S. *J. Phys. Chem.* **1985**, 89, 5133; (b) Ofer, D.; Wrighton, M. S. *J. Amer. Soc.* **1982**, 110, 4467.
9. (a) Galizzioli, L.; Tantardini, F. Trasatti, S. J. *Appl. Electrochem.* **1975**, 5, 203; (b) Pizzini, S.; Buzzana, G.; Mari, C.; Rossi, K.; Torcho, S. *Mat. Res. Bull.* **1972**, 7, 449.
10. Sze, S. M. *Physics of Semiconductor Devices*, 2nd Edition; Wiley-Interscience: New York, **1981**.
11. Birss, V.; Myers, R.; Angerstein-Kozłowska, H.; Conway,

- B. E. J. *Electrochem. Soc.* **1984**, 131, 1502.
12. (a) Kim, K.S.; Winograd, N. *J. Catal.* **1974**, 35, 66;  
(b) Folkesson, B. *Acta Chem. Scand.* **1973**, 27, 287.
  13. (a) Trasatti, S.; Buzzanca, G. *J. Electroanal. Chem.* **1971**, 29, App. 1. (b) Galizzioli, D.; Tantardini, F.; Trasatti, S. *J. Appl. Electrochem.* **1974**, 4, 57.
  14. Hadzi-Jordanov, S.; Angerstein-Kozlowska, H.; Vukovic, M.; Conway, B. E. *J. Electrochem. Soc.* **1978**, 125, 1473.
  15. Burke, L. D.; Mulcahy, J. K.; Venkatesan, S. *J. Electroanal. Chem.* **1977**, 81, 339.
  16. Feldberg, S. W. *J. Amer. Chem. Soc.* **1984**, 106, 4671.
  17. Murray, R.W. in *Electroanalytical Chemistry*, Vol. 13; Bard, A.J., (Ed), Marcel Dekker; New York, **1984**, p. 191.
  18. Lewis, T. J.; White, H. S.; Wrighton, M. S. *J. Amer. Chem. Soc.* **1984**, 106, 6947.
  19. Burke, L. D.; Twomey, T. A. M. *J. Electroanal. Chem.* **1984**, 162, 101.
  20. Burke, L. D.; Whelan, D. P. *J. Electroanal. Chem.* **1984**, 162, 121.
  21. Burke, L. D.; O'Sullivan, E. J. M. *J. Electroanal. Chem.* **1981**, 129, 133.
  22. Burke, L. D.; Lyons, M. E.; Whelan, D. P. *J. Electroanal. Chem.* **1982**, 139, 131.
  23. El Wakkad, S. E. S.; Shams El Din, A. M. *J. Chem. Soc.* **1954**, 3094.
  24. Burke, L. D.; Healy, J. F. *J. Electroanal. Chem.* **1981**,

124, 327.

25. Burke, L. D.; Lyons, M. E. G. In *Modern Aspects of Electrochemistry*, No. 18; White, R. E., Bockris, J. O'M., Conway, B. E., Eds.; Plenum: New York, **1986**; p 169.
26. Laviron, E. In *Electroanalytical Chemistry*, Vol. 12; Bard, A. J., Ed.; Marcel Dekker: New York, **1982**; p 53.
27. Rishpon, J.; Gottesfeld, S. J. *Electrochem. Soc.* **1984**, 131, 1960.
28. (a) Belanger, D.; Wrighton, M.S. *Anal. Chem.*, **1987**, 59, 1426; (b) Shu, S. F.; Wrighton, M. S. *J. Phys. Chem.* **1988**, 92, 5221; (c) Shu, S. F.; Wrighton, M. S. *ACS Symposium Series*, No. 378; Soriaga, M. P., Ed.; ACS, Washington, **1988**.
29. Lofton, E. P.; Thackeray, J. W.; Wrighton, M. S. *J. Phys. Chem.* **1986**, 90, 6080; (b) Jones, E. T. T.; Chyan, O. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1987**, 109, 5526.
30. Schloh, M. O.; Wrighton, M. S. *Chemistry of Materials*, submitted (following article in this issue).

# FIGURE CAPTIONS

**Figure 1.** Scanning electron micrograph of  $\text{RuO}_x$  deposited onto a Pt electrode.

**Figure 2** Scanning Auger element map of Ru (top) and scanning electron micrograph (bottom) of a microelectrode array in which the central four electrodes are derivatized with  $\text{RuO}_x$  and the other four electrodes kept underivatized

**Figure 3.** Cyclic voltammetry of glassy carbon/ $\text{RuO}_x$  in pH 7, 0.05 M Na(phosphate)/0.3 M  $\text{NaNO}_3$  solution. Scan rate: 10 mV/s.

**Figure 4.** UV-vis absorption (top) and difference absorption (bottom) spectra for  $\text{SnO}_2/\text{RuO}_x$  electrode potentiostatted at -0.6, -0.5, -0.4, -0.3, -0.2, -0.1, 0.0, 0.1, 0.2, 0.3, and 0.35 V vs. SSCE. The  $\text{RuO}_x$  film thickness is  $\sim 1300 \text{ \AA}$ .

**Figure 5.** Half wave potential of  $\text{RuO}_x$  as a function of pH.  
 ●: C/ $\text{RuO}_x$ ; ▲: Pt/ $\text{RuO}_x$  (both in 0.05 M buffer/1.0 M NaCl).  
 x: Pt/ $\text{RuO}_x$  in 0.05 M buffer/1.0 M  $\text{NaNO}_3$ . Extrapolation of this line gives  $E^{0'} = +0.50 \text{ V}$  vs. SSCE at pH = 0.

**Figure 6.** Peak anodic current for the  $\text{RuO}_x$  voltammetric wave at a Pt/ $\text{RuO}_x$  electrode. Solutions are 0.05 M buffer/1.0 M  $\text{NaNO}_3$ .



**Figure 7.** Cyclic voltammograms at pH 7.5 of the four individual adjacent  $\text{RuO}_x$ -connected microelectrodes and of the four microelectrodes driven together.

**Figure 8.** Resistance of  $\text{RuO}_x$ -connected microelectrodes as a function of  $V_G$  at pH 7.5. The data was obtained by scanning one electrode  $\pm 25$  mV about  $V_G$  at 50 mV/s. The resistance is plotted on a logarithmic scale.

**Figure 9.**  $I_D$  vs. time for a  $\text{RuO}_x$ -based transistor at pH 7.5 as  $V_G$  is stepped repetitively every 20 s from -0.50 to +0.05 V vs. SSCE and back.  $V_D = 100$  mV.

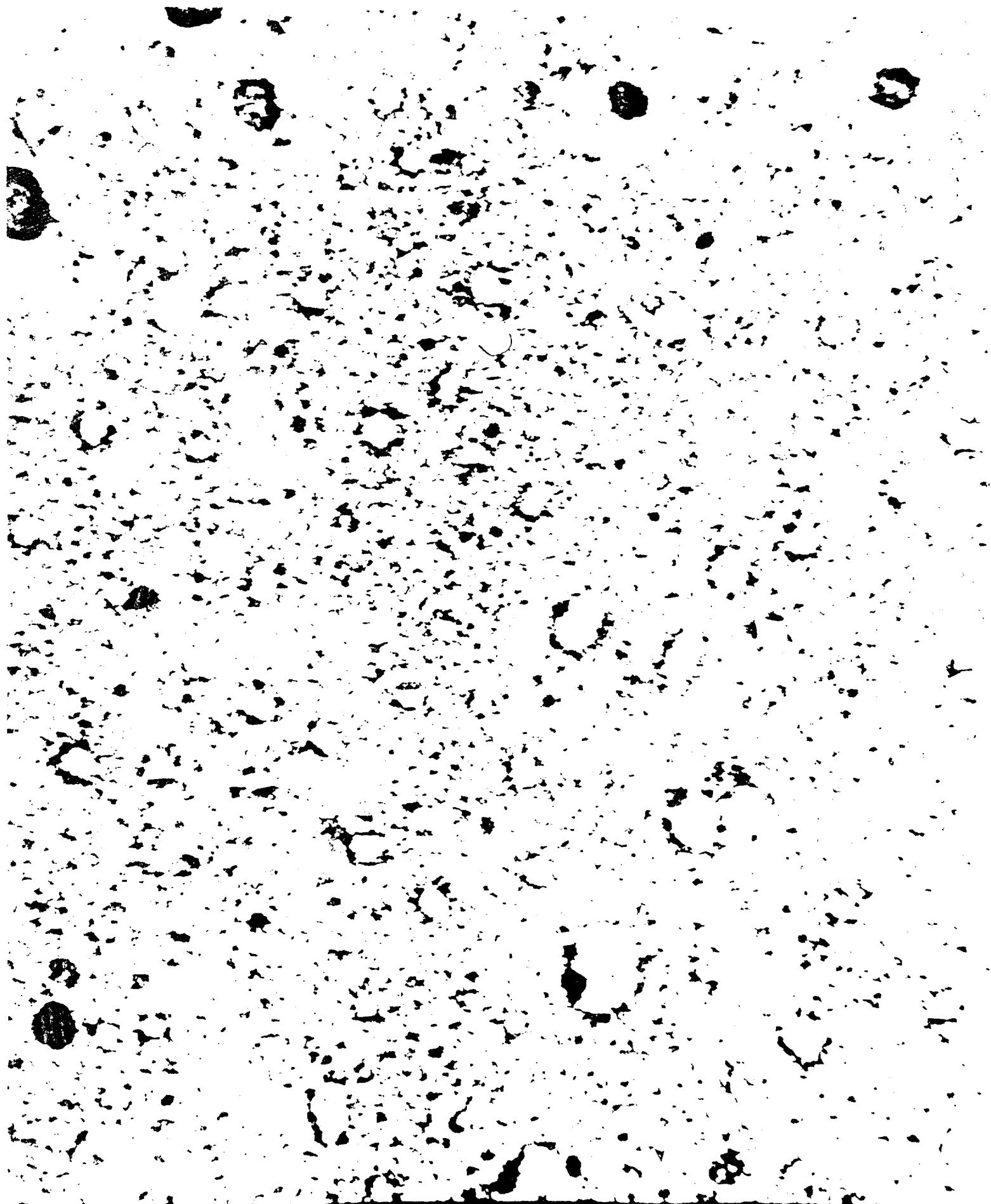
**Figure 10.** Simultaneous measurement and phase relationship of  $V_G$ ,  $I_G$ , and  $I_D$  for a  $\text{RuO}_x$ -based microelectrochemical transistor at pH 7.0 as  $V_G$  is repetitively swept linearly from -0.35 to +0.05 V vs. SSCE and back at a frequency of 0.1 Hz.  $V_D = 100$  mV.

**Figure 11.** pH dependence of steady state  $I_D$  vs  $V_G$  (at fixed  $V_D = 100$  mV) for a  $\text{RuO}_x$ -based microelectrochemical transistor.

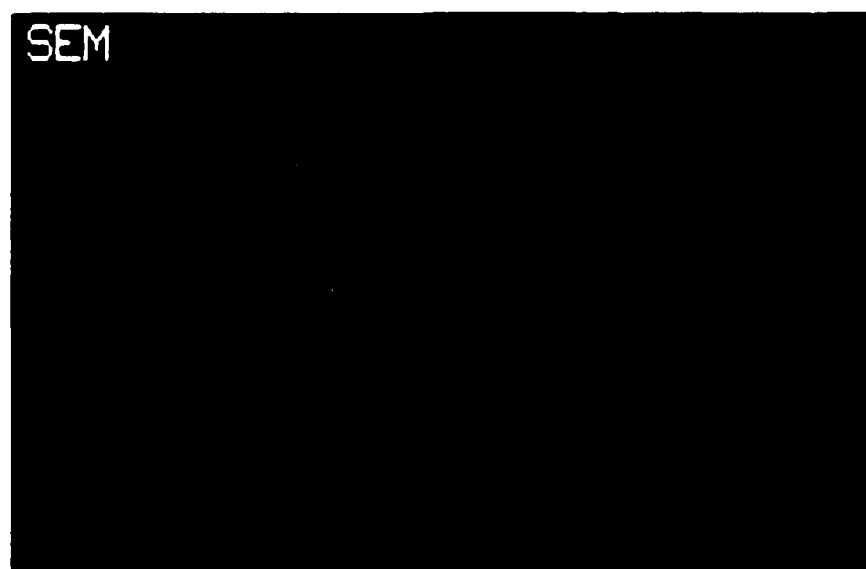
**Figure 12.**  $I_D$  vs. time for a  $\text{RuO}_x$ -based microelectrochemical transistor as the pH of a continuously

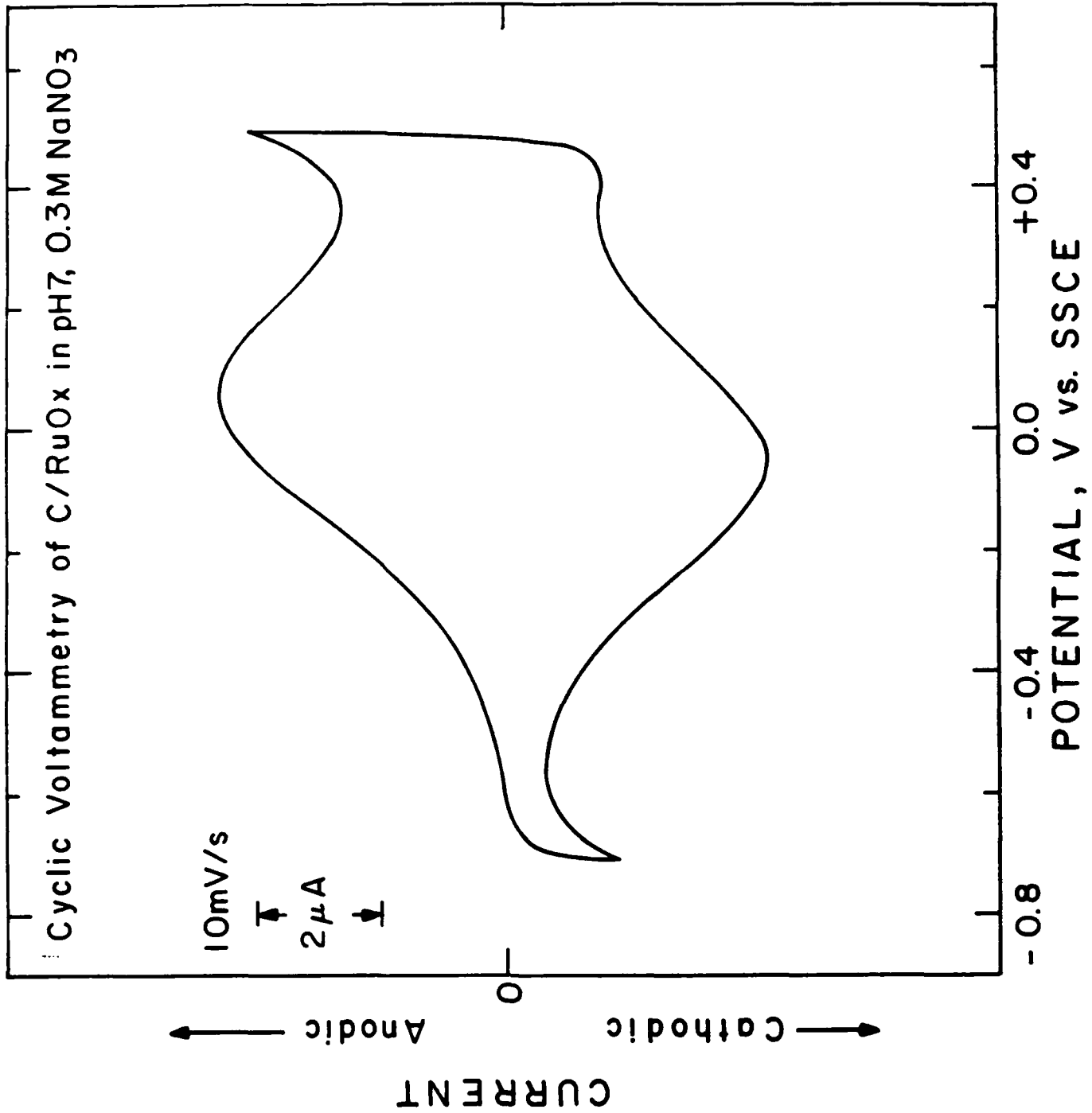
flowing stream is varied from 5.5 to 7.3.  $V_G = 0.0$  V vs. SSCE and  $V_D = 100$  mV.

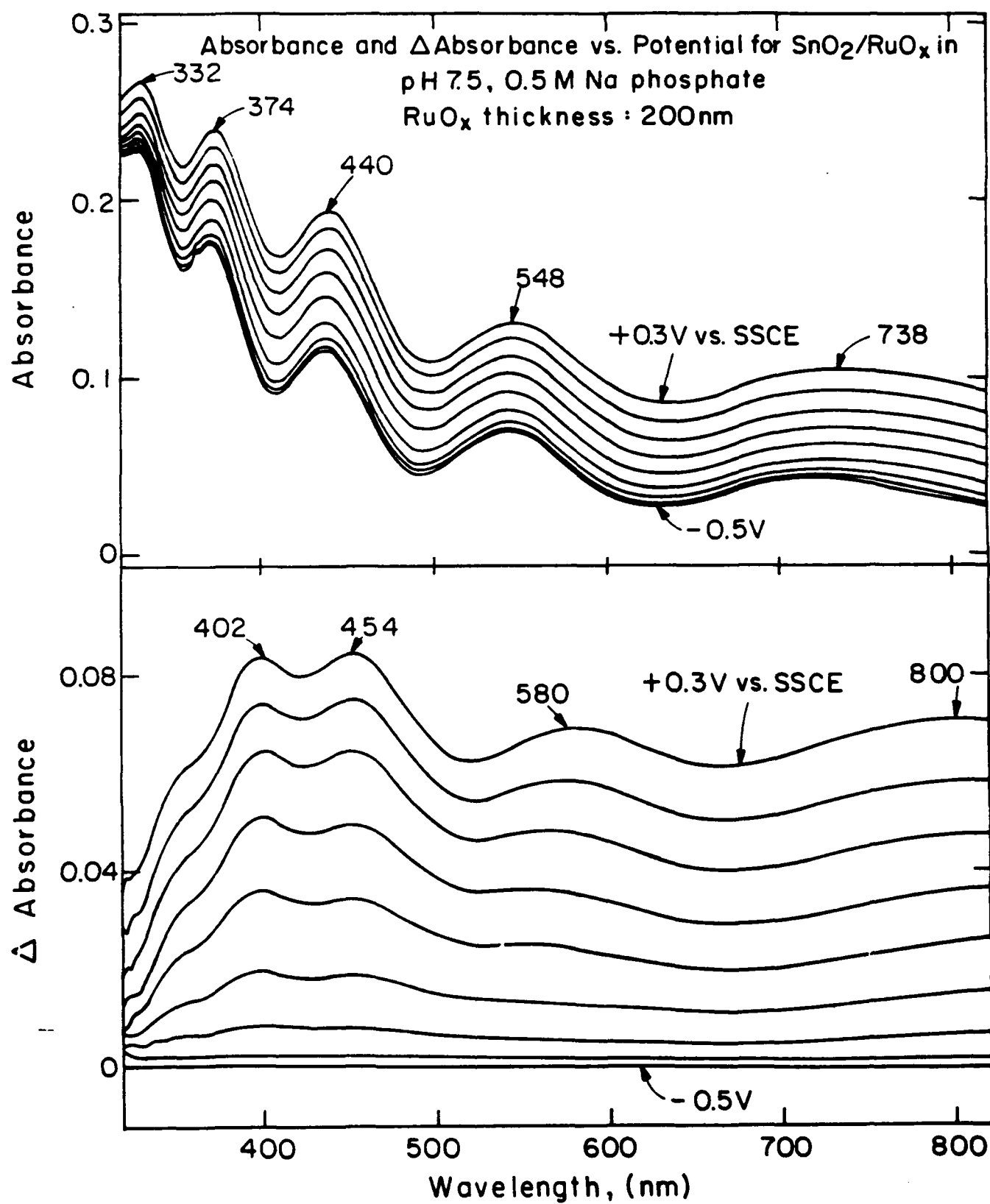
**Figure 13.** Proposed structure of  $\text{RuO}_x$ . Oxoruthenium moieties surround a porous ruthenium-oxygen lattice.

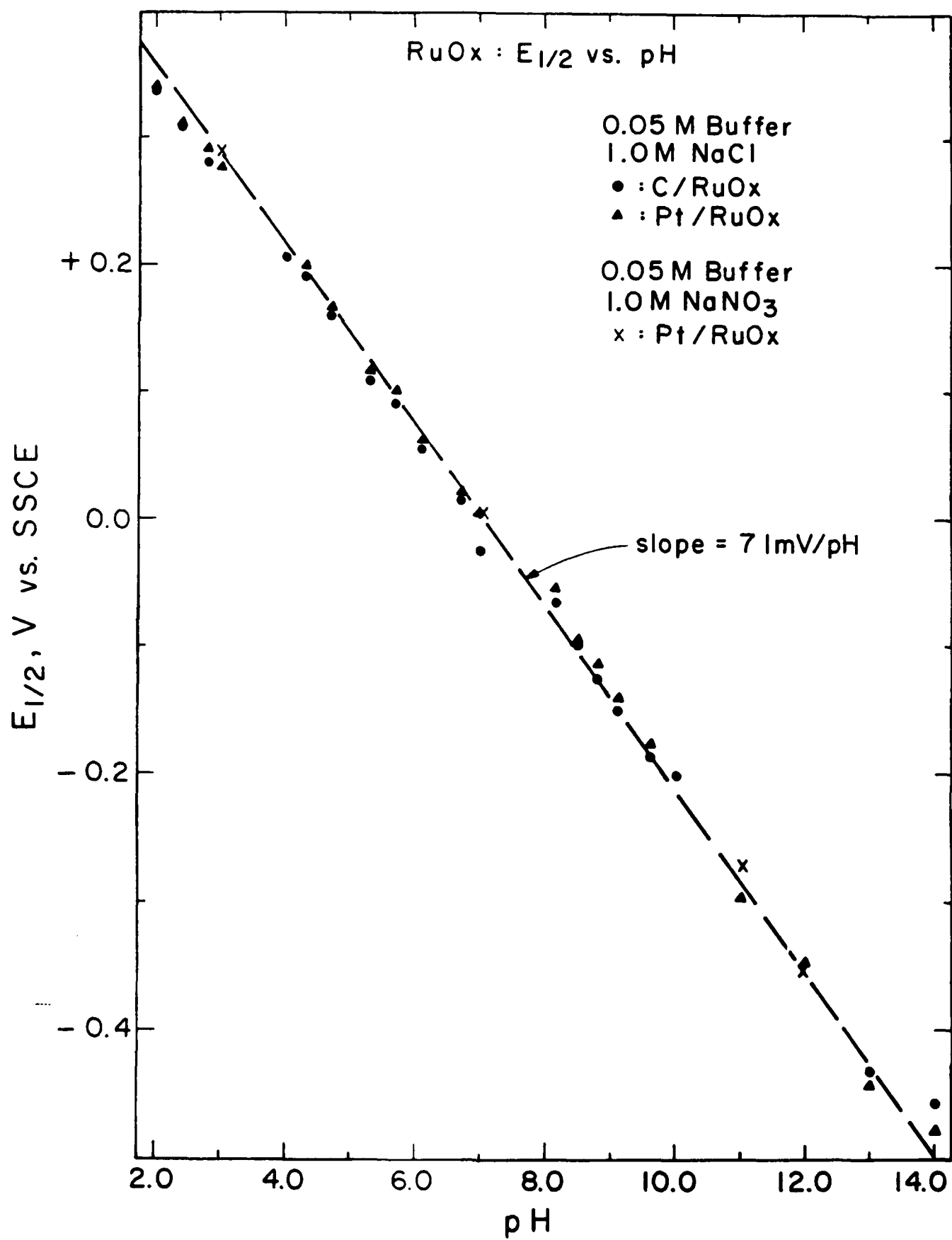


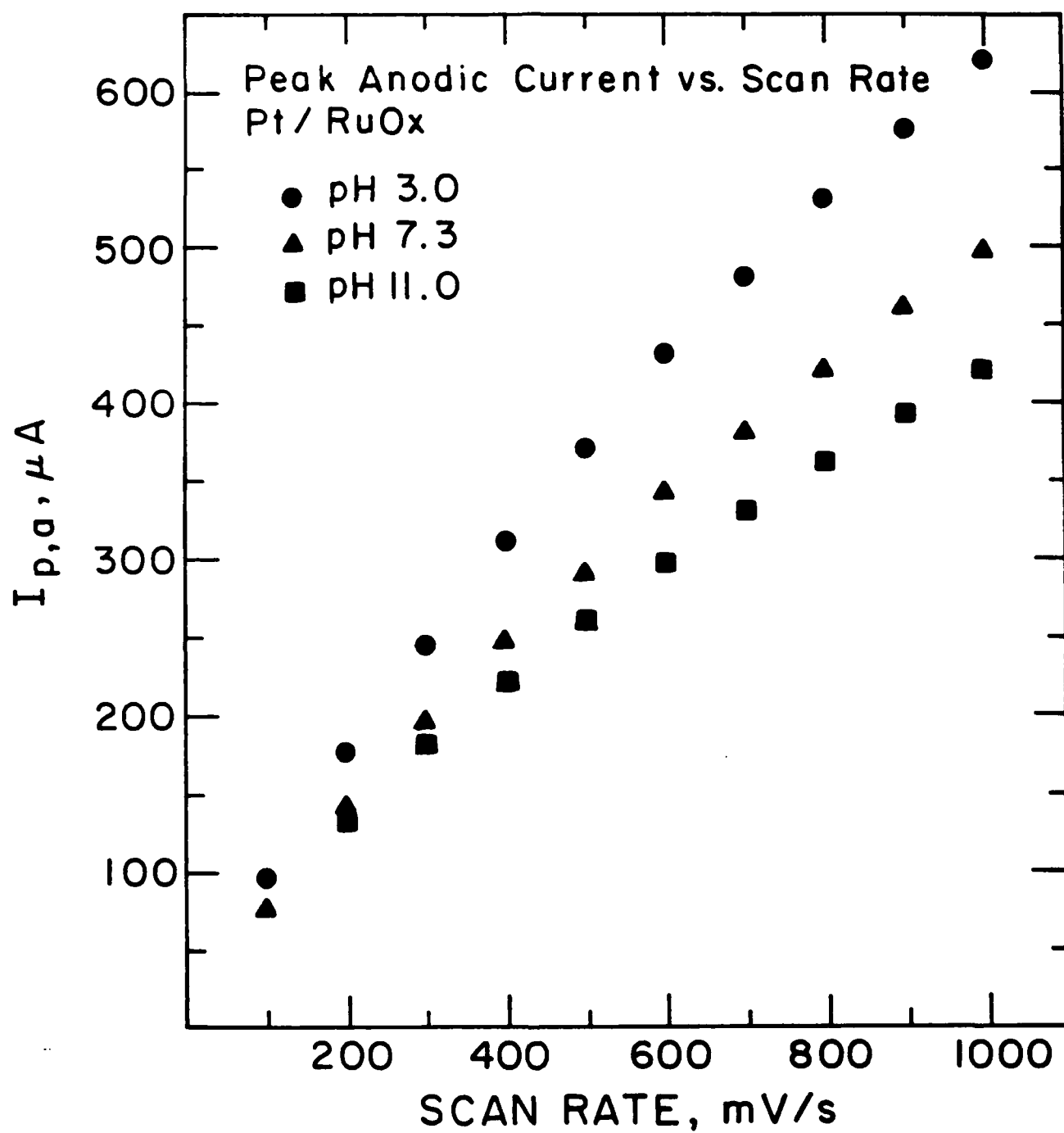
| 600 nm |





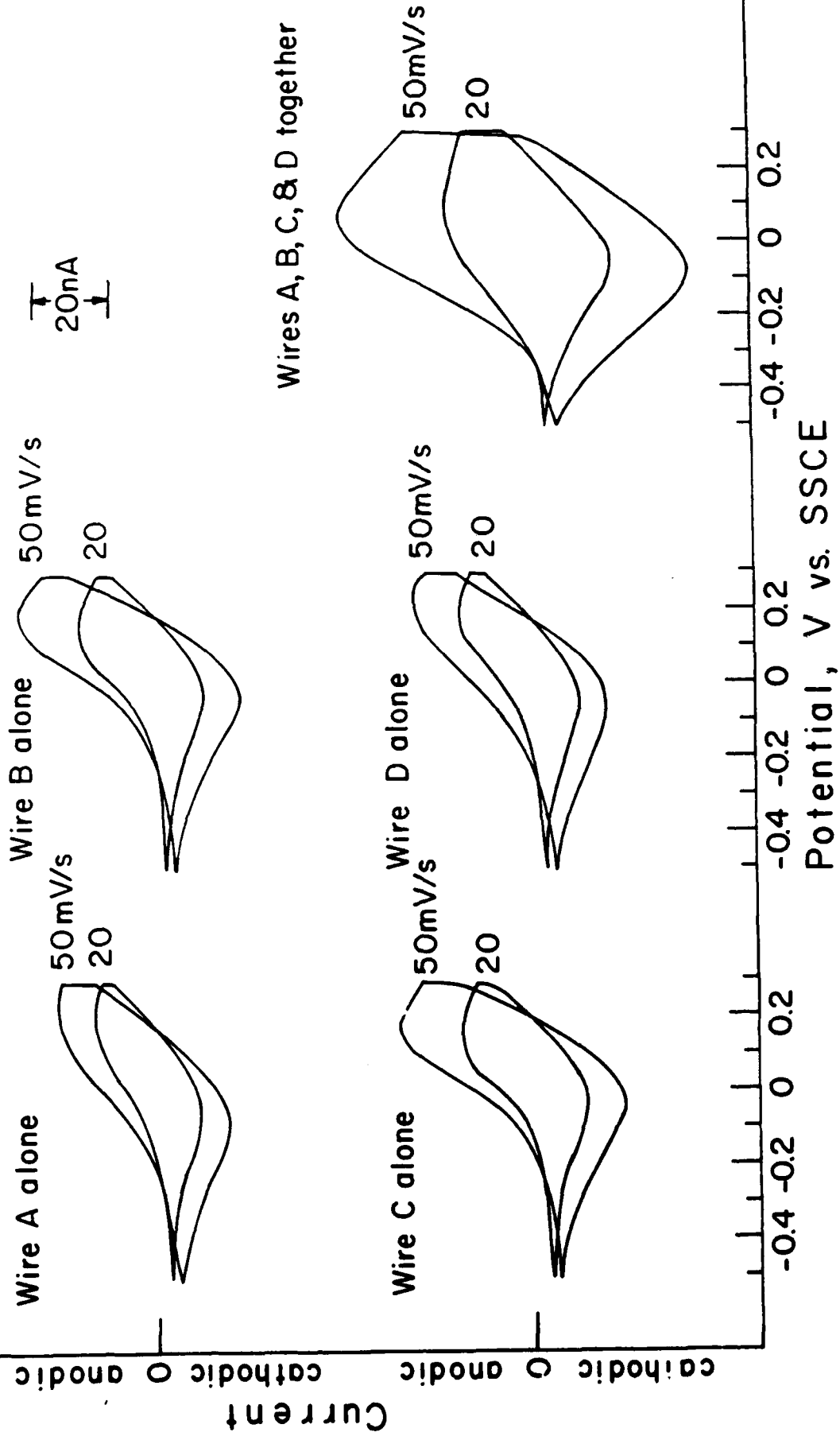


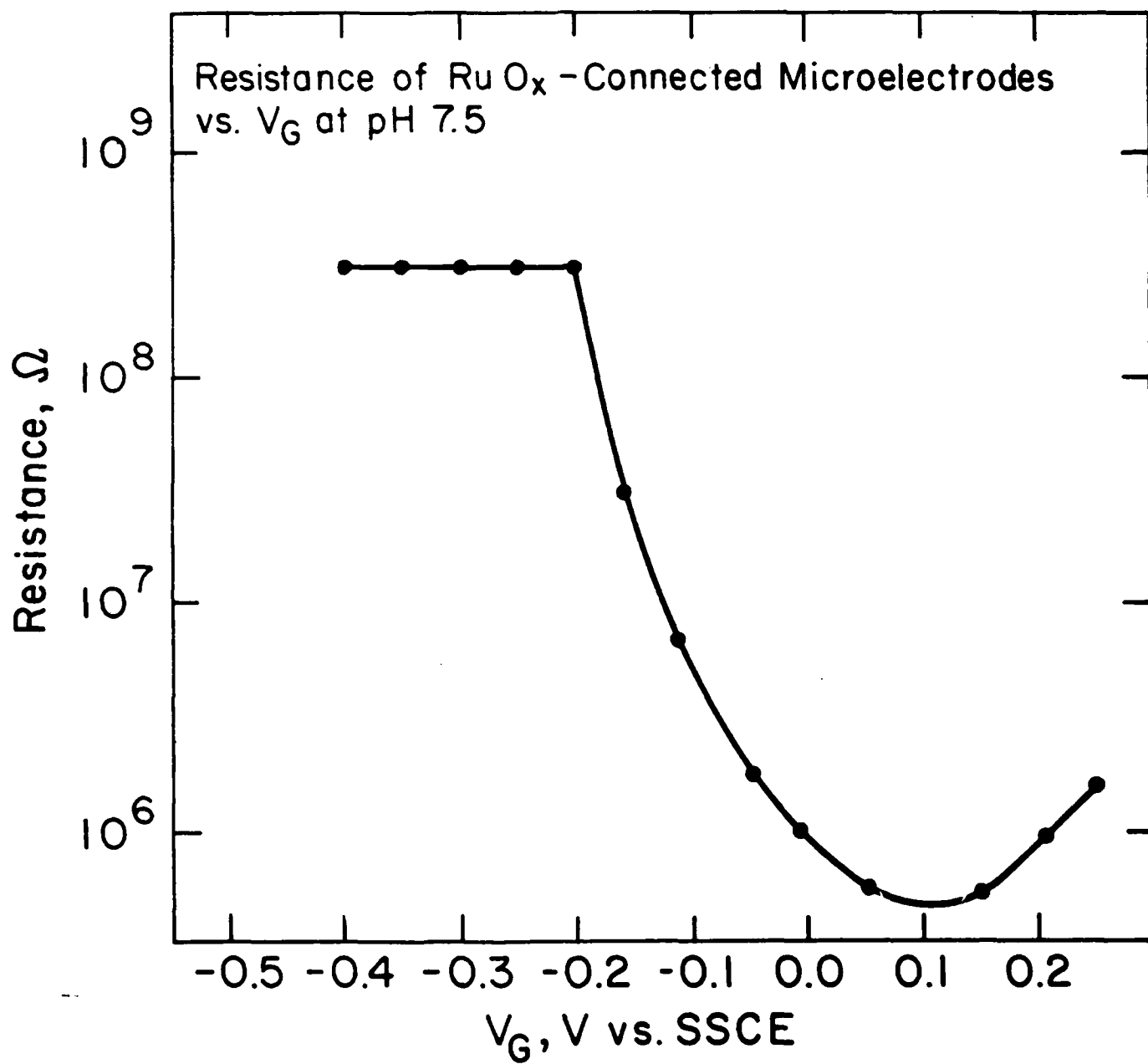






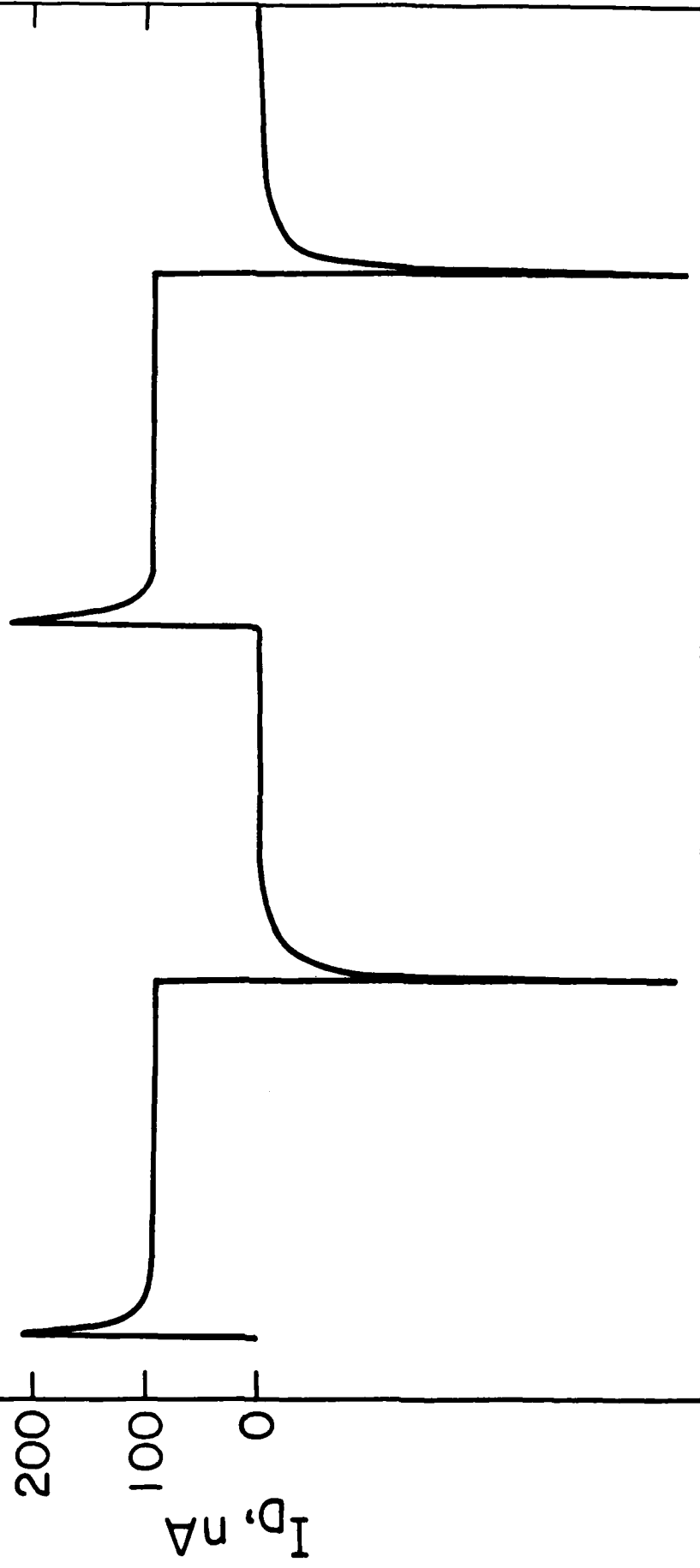
# Scan Rate Dependence of the Cyclic Voltammetry of RuO<sub>x</sub> - Connected Microelectrodes at pH 7.3





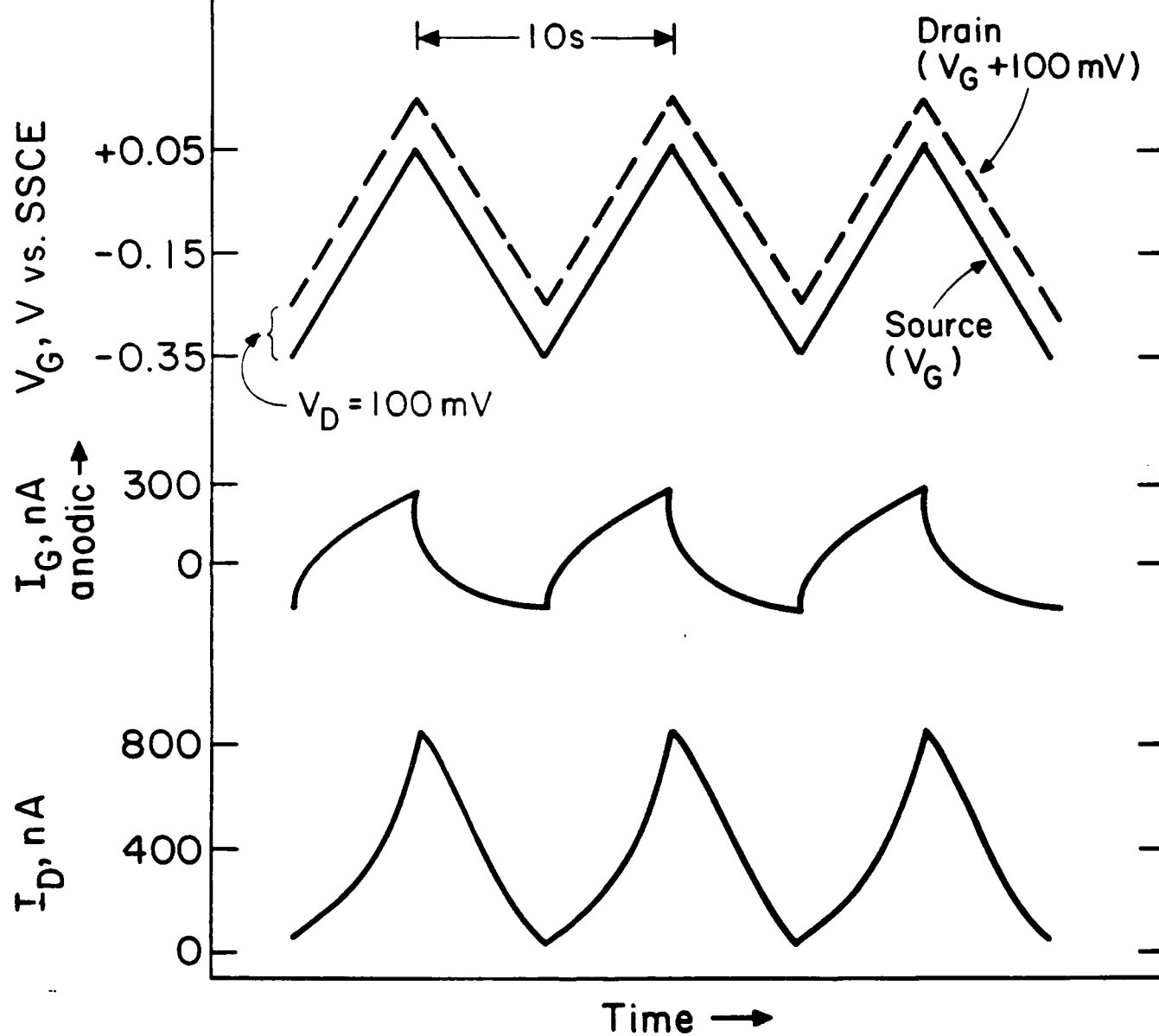
$I_D$  vs. Time for a  $\text{RuO}_x$  - Based Transistor at pH 7.5 for a Potential Step from  $-0.5$  to  $+0.05\text{V}$  vs. SSCE.  $V_D = 100\text{mV}$

20s



Time →

Phase Relationship Between  $V_G$ ,  $I_G$ , and  $I_D$  for a  $\text{RuO}_x$ -Based Transistor at pH 7.0



Drain Current Response vs. Time for a RuOx Transistor Upon Alternate  
Cycling of a pH 5.5/7.3 Effluent Stream.  $V_G = 0.0\text{ V}$  vs. SSCE,  
 $V_D = 0.1\text{ V}$ , Flow Rate =  $2.0\text{ mL/min}$ .

